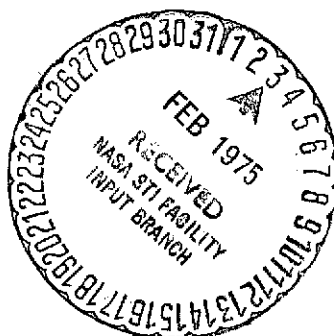


PREPARATION OF SINTERED OXIDES OF HOLLANDITE TYPE
STRUCTURE ($K_xMg_{x/2}Ti_{8-x/2}O_{16}$) AND THEIR IONIC
CONDUCTION

Takehiko Takahashi and Katsumi Kuwabara

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16. Abstract Ionic conduction in sintered oxides with hollandite type structure $\text{K}_{1-x}\text{Mg}_x/2\text{Ti}_8\text{O}_{16}$, which have tetragonal lattice and involve tunnels along the c axis, was investigated. Degree of sintering was defined by the ratio of apparent density of theoretical X-ray density. When K_2CO_3 , MgO and TiO_2 were fired at 1200°C for 5 hr after pre-firing at 950°C for 10 hr, the degree of sintering reached 85~90%. From the results of the powder X-ray diffractions and fluorescence X-ray analyses and lattice constants, the composition range of tetragonal single phase was determined to $1.6 \leq x \leq 2.0$. The tablets of about 11 mm in diameter and 2 mm in thickness were prepared from the sintered single phase and their A.C. conductivities at 10 kHz were measured using a pair of gold plate electrodes in the temperature range from 200°C to 400°C. The conductivities were found to increase from the order of 10^{-5} to 10^{-4} mho·cm ⁻¹ with the decrease of x. The species contributing to the ionic conduction in the sintered specimens of single phase was clarified to be potassium ion.			
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STRUCTURE ($K_xMg_{x/2}Ti_{8-x/2}O_{16}$) AND THEIR IONIC
CONDUCTION

Takehiko Takahashi and Katsumi Kuwabara*

ABSTRACT. Research was conducted on ionic conduction of sintered oxides of the hollandite type, $K_xMg_{x/2}O_{16}$, having a tetragonal lattice and involving tunnels along the c axis. The degree of sintering was defined as the ratio of apparent density and the theoretical x-ray density. When K_2CO_3 , MgO and TiO_2 were fired at $1200^\circ C$ for five hours after prefiring at $950^\circ C$ for 10 hours, the degree of sintering reached 85-90%. From the results of the powder x-ray diffractions and fluorescent x-ray analysis and lattice constants, the composition range of tetragonal single phase was determined to be $1.6 \leq x \leq 2.0$. Tablets, about 11mm in diameter and 2mm in thickness, were prepared from the sintered single phase, and the 10kHz AC conductivity of the specimens was measured with gold-plated electrodes in the temperature range from $200^\circ C$ to $400^\circ C$. Conductivity was found to increase from 10^{-5} to $10^{-4} \text{ mho.cm}^{-1}$ as x decreased. Through comparison, according to Tubandt's method, of weight changes of tablets before and after electrolysis, it was clarified that the conduction seed of the sintered specimens of single phase was K^+ ion. The correlation of K^+ ion conductivity and hollandite type structure was briefly reviewed.

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Surface

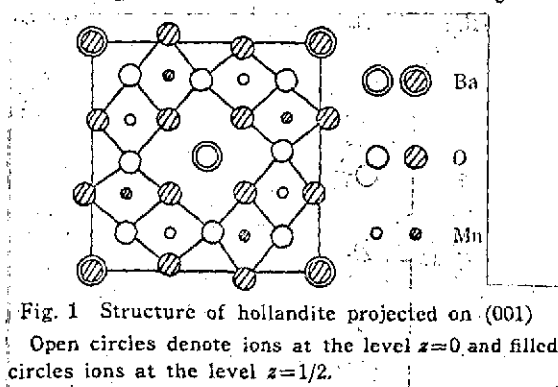
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** Numbers in the margin indicate pagination of original foreign text.

1. Preface

It is well known that several compounds formed around α -AgI manifest a high Ag^+ ion conductivity at room temperature [1], which is believed due to the average structure or the three-dimensional, disarrayed lattice seen in α -AgI. The correlation of such ion conductivity and the somewhat disarrayed crystalline structure [2] presents a very interesting topic in research on high ion conductivity.

The compound involved in this research is expressed in the general formula, $\text{K}_x\text{Mg}_{x/2}\text{Ti}_{8-x/2}\text{O}_{16}$, and is similar in structure [3] to hollandite, $\text{Ba}_x\text{Mn}_{x/2}\text{II}\text{Mn}_{8-x/2}\text{IV}\text{O}_{16}$, a type of manganese/ Figure 1 is a projection of hollandite on (001). [4] Manganese is located in the center of the oxygen-containing octahedron. This octahedron, by means of a common perimeter, forms a double octahedron which in turn forms a chain by having common corners. Barium is bounded by the slightly distorted eight oxygen cubes along the border and four on the same plane as barium and parallel with this paper. The basic structure extends in the direction of the c axis perpendicular to the paper and forms a so-called tunnel. [5] $\text{K}_x\text{Mg}_{x/2}\text{Ti}_{8-x/2}\text{O}_{16}$ is equivalent to a rearrangement of barium in hollandite with potassium, and of manganese with magnesium and titan. KCl, of rock-salt structure, indicates a K^+ ion conductivity of only about $10^{-7} \text{ mho} \cdot \text{cm}^{-1}$ at 300°C , [6] but $\text{K}_x\text{Mg}_{x/2}\text{Ti}_{8-x/2}\text{O}_{16}$, of the hollandite type structure, can be expected to manifest a high K^+ ion conductivity through its tunnels.



2. Method of Experiment

2.1. Preparation of Sinter Specimen

K_2CO_3 , MgO and TiO_2 were measured and removed in the range of $x=1.4 - 2.2$ of $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ and dried for several hours at $100^\circ C$ after wet blending with toluene. After being formed into a disc at pressure of $2 \text{ ton}\cdot\text{cm}^{-2}$, it was prefired in air for 10 hours at $950^\circ C$ and pulverized into 300-mesh size powder. A portion of this material was used for x-ray analyses, and the rest for firing. The sinter was obtained by applying pressure with a rubber press, $3 \text{ ton}\cdot\text{cm}^{-2}$, to prefired powder; tablets were made 11 mm in diameter and about 2-3 mm in thickness, after which heat was applied from 2-10 hours in air at $1200-1400^\circ C$.

2.2. X-Ray Analyses

In qualitative analysis, copper was used on the anti-cathode and powder x-ray diffractions were obtained under the ordinary method. Measurement of lattice constant was conducted more than 10 times on specimens of the same composition, using silicon as the internal standard. Further, a fluorescent x-ray analysis, using a scientific electrical instrument, GF-SX, was conducted. The target at this time was chrome. Potassium and titan were also studied; in the former, the EDDT proportional counter system, and in the latter, the LiF scintillation counter system were applied. /1884

2.3 Review of Ion Conductivity

Conductivity of the specimen was determined by polishing the specimen with a No. 1200 emery paper, then clamping it with gold-plated electrodes and heating for about $200-400^\circ C$ in air.

The instrument used was a Yokogawa Electric AC impedance bridge, with frequency at 10kHz. To clarify the ion seed for conduction, Tubandt's electrolysis method [7] was employed to determine the weight changes in the anode and cathode sides of the specimen tablet.

3. Results and Observations

3.1 Single phase range of sinters

In analyzing the crystalline structure of $K_xMg_{x/2}Ti_{8-x/2}O_{16}$, Bayer and his colleagues used KNO_3 as potassium base and only furnished data on sintering conditions: 1000°C at 20 hours, $x=2.0$. [3] Therefore, we used K_2CO_3 for potassium base and studied the property of sinters under conditions different from that of composition x .

Figure 2 shows a x-ray diffraction pattern of a typical composition of prefiring and firing specimens. Circle denotes the tetragonal defraction curve being sought. In the prefiring condition, solid phase reaction (goal) has advanced considerably, and in each composition, there are numerous defraction curves reflecting low temperature and unknown phases of TiO_2 . In the firing specimen, $x=1.4$, there was a very simple defraction; except for the high temperature phase of TiO_2 . In $x=1.8$, there was only a single phase defraction equivalent to the tetragonal phase, and $1.6 \leq x \leq 2.0$ produced a similar refraction. In $x=2.2$, the defraction curve indicated a presence of an unknown phase in the vicinity of 29°. Such defractions were observed also in specimens fired at 1400°C.

Figure 3 shows the lattice constant of specimens fired at 1200°C. While the c axis undergoes a gradual change, the a axis

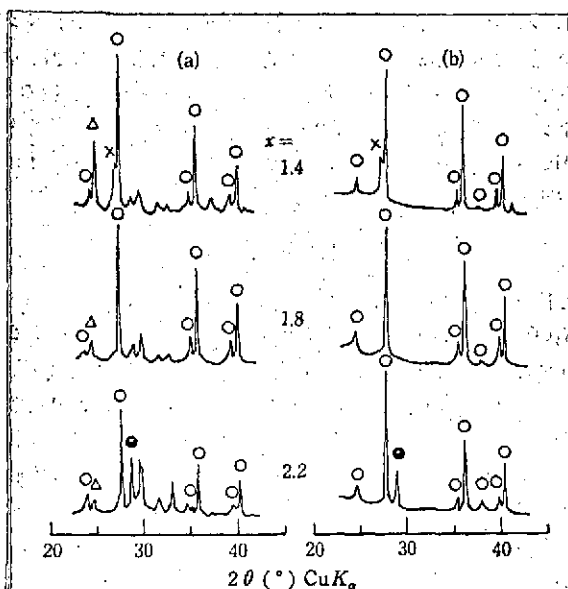


Fig. 2 X-ray diffraction pattern of $K_xMg_{x/2}Ti_{3-x/2}O_{10}$

- (a) : Obtained from prefiring at 950°C for 10 hr
 (b) : Obtained from firing at 1200°C for 5 hr
 ○ : Tetragonal phase
 △ : Low temperature phase of TiO_2
 × : High temperature phase of TiO_2
 ● : Unknown phase

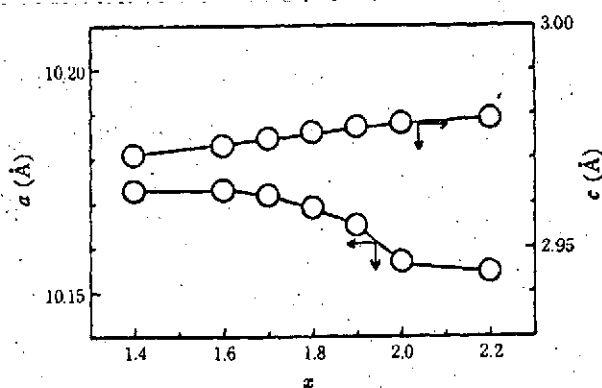


Fig. 3 Lattice parameter of $K_xMg_{x/2}Ti_{3-x/2}O_{10}$ obtained from firing at 1200°C for 5 hr after prefiring at 950°C for 10 hr

bends at $x=1.6$ and 2.0 . The Vegard law cannot be applied here because it is not of a simple dual-system. Since changes in the a axis also occur in the ternary system in this manner, there are indications that boundaries exist in the composition $x=1.6$ and 2.0 .

With respect to the formation of sinters, there is the problem of evaporation of potassium during firing. Using as standard specimen the blended powder before it is subjected to prefiring, a comparison of sinters was effected with fluorescent x-ray. The composite error due to evaporation at time of firing was negligible at 1200°C, but rose several percent at 1400°C. Further, almost no difference was noted among tablets covered with powders of the same composition and those uncovered at the time of firing.

As a result of the x-ray analysis, the range of tetragonal single phase was clarified to be $1.6 \leq x \leq 2.0$. In discussions below, we will use sinters obtained after 5 hours at 1200°C so that evaporative problems can be ignored.

3.2 Sintering properties

No appropriate value for measuring the degree of sintering has yet been established. Accordingly, such indirect terms as apparent density, ring density, contraction rate or pore rate are used.

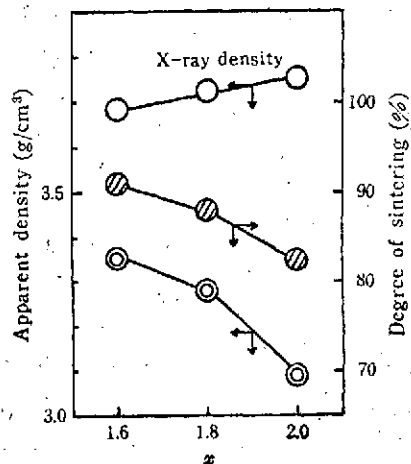


Fig. 4 Apparent density, X-ray density are plotted against sintering of $K_xMg_{x/2}Ti_{3-x/2}O_{16}$

Under the ordinary method using picknometers to measure density, serious experimental errors may develop, depending on the degree of fine pulverization of the sinter and the de-airing process. Consequently, we shall discuss the matter of sintering from the standpoint of apparent density which allows for simpler measurement and fewer experimental errors.

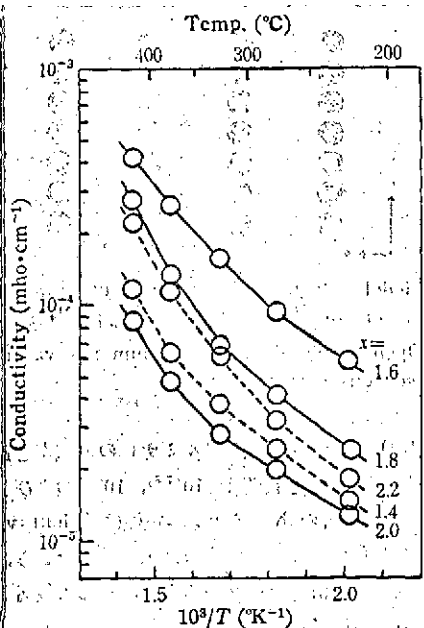


Fig. 5 Temperature-dependence of conductivity of sintered $K_xMg_{x/2}Ti_{3-x/2}O_{16}$

Figure 4 shows the apparent density in the range of the single phase, and the theoretical x-ray density based on the lattice constant of Figure 3. The apparent density was obtained from dimensions and weight of tablets for use in measuring conductivity. The use of monocrystalline density would have been ideal. However, as monocrystals were unavailable and since the lattice volume changes slightly, depending on the sintering conditions, the theoretical x-ray density was used as the standard density. The ratio of apparent

density as a measurement of sintering and the theoretical x-ray density was taken and plotted to be 85-90%, as shown in Figure 4 [8].

3.3 Conductivity

Figure 5 reflects the temperature dependence of conductivity within the range of 200-400°C. Single phase is shown by a line, while the blended phase is shown by a broken line. As can be observed, both lines are not straight; however, the higher the degree of sintering as shown in Figure 4, the greater propensity toward a straighter line. Figure 6 shows the relation between conductivity and composition. In a $x < 1.6$ blending phase, the value is smaller than $x = 1.6$, whereas in the $x > 2.0$ blending phase, it is larger than $x = 2.0$. A simple relation can be seen in the single phase relative to composition.

Singer and his colleagues, calculating the AC conductivity of $K_{1.6}Mg_{0.8}Ti_{7.2}O_{16}$ on the basis of dielectric and capacity measurements, reported a value having a very wide spread of about $4 \times 10^{-7} \sim 2 \times 10^{-2} \text{ mho} \cdot \text{cm}^{-1}$ at 25°C. [9] Since our measured values could not be compared to theirs because theirs were not a direct measurement of conductivity, the difference of value of specimens was excessively great, and virtually no study of conductivity had been made, we prepared a sinter according to their method for reference's sake and measured its conductivity, the results of which are shown in Figure 7. Conductivity was smaller than the value attained by us as shown in Figure 5; the dependence on the composition was also relatively smaller and was within the oblique line.

3.4 Ion seed for conduction

For the purpose of determining whether the foregoing conductivity is due to ions or electrons (including positive hole)

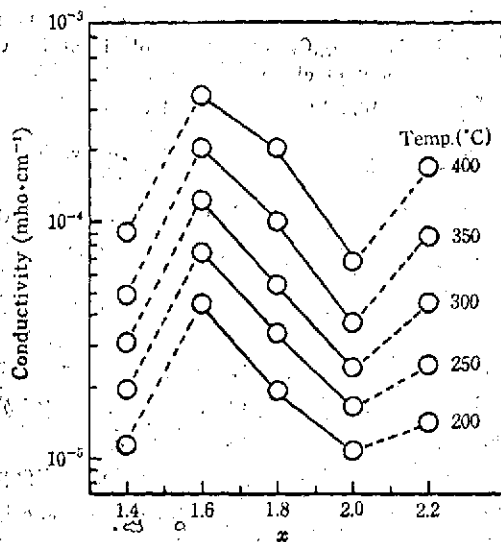


Fig. 6 Relation between the total conductivity and potassium content of $K_xMg_{x/2}Ti_{2-x/2}O_{10}$

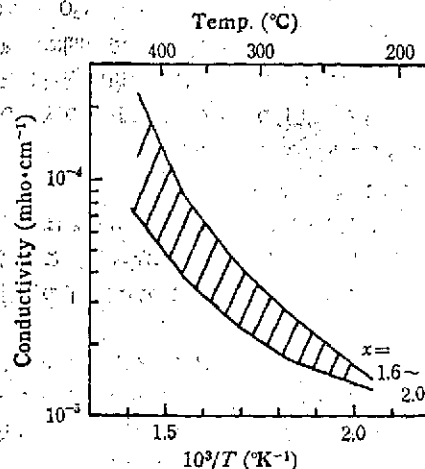
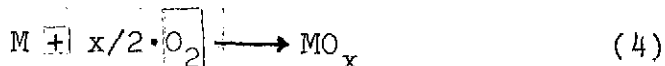
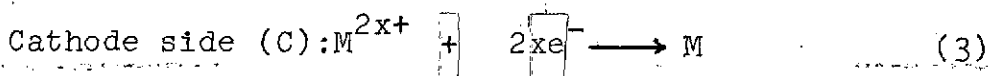
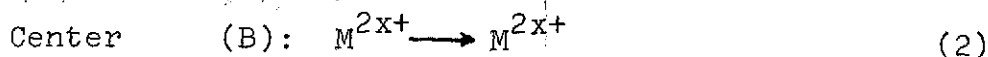
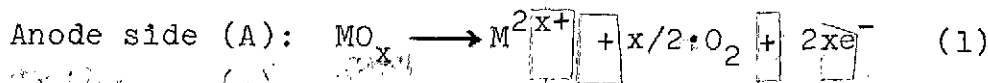


Fig. 7 Conductivity of the specimens made by the NASA method, namely by the two firings at 1100°C for 2 hr and 1200°C for 2 hr in air within packing powder of the same composition

and, if ions, which are responsible, we stacked three sintering tablets, placed them in contact with gold-plated electrodes and subjected them to electrolysis with 100-500 μ A current at 300°C. Weight changes of each tablet before and after electrolysis were measured.

Assuming that certain catheon (M) is involved in conduction, oxygen gas will be generated at the anode side because of electrolysis, and the catheon will move to the cathode side, according to the formula below. At the cathode side, the metallic element formed as a result of electrical discharge of the conducting catheon will react with oxygen and be converted into an oxide.



Hence, the tablet on the anode side should undergo weight reduction equal to the weight of the oxide from the conducting /1886 cathode, with a corresponding weight increase on the cathode side. There probably is no weight change when only an oxygen ion or electron is involved in conduction.

Table 1 Weight change of the tablets of specimen $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$ after electrolysis at 300°C (Amount of electricity: 22.5 g)

Tablet	Observed value	Weight change of tablet (mg)			
		Calculated value for various charge carriers			
		K^+	Mg^{2+}	Ti^{4+}	O^{2-}
A	-10.7	-11.00	-4.68	-4.67	0
B		0	0	0	0
C	+12.2	+11.00	+4.68	+4.67	0

Table 1, for example, reflects the observed value of weight changes in the case of $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$, and calculated value of weight change for a hypothetical conduction ion seed charged with electrical current of 22.5 Coulomb. The observed

value is in harmony with the calculated value of K^+ ion hypothesized as the conducting seed. The weight on the cathode side is heavier than the calculated value. The reason for this, when considering the solubility and strong basicity of the deduced material on the cathode side, is believed due to the fact that a part of the oxides, K_2O or KO_2 formed under Formula (4) was converted into hydrate or carbonate after absorbing moisture in the air or carbon dioxide during the period between electrolysis and tablet weighing. It is evident from the foregoing that the ion seed of these specimens are K^+ ion.

3.5 K^+ ion conductivity and tunnel structure

As initially anticipated, it became clear that $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ showed an extremely large K^+ ion conductivity. Let us briefly discuss this high ion conductivity and the hollandite type tunnel structure.

By tunnel structure is meant a relatively loosely positioned lattice elongated one-dimensionally. For ions to migrate within

this tunnel, it would be better if the diameter of the tunnel is as large as can be tolerated by the lattice. The diameter of the tunnel that can be obtained experimentally is the length of the a axis. As is shown in Figure 3, the smaller the composition x , the bigger the a and larger the diameter of the tunnel.

In $K_xMg_{x/2}Ti_{8-x/2}O_{16}$, there are two places in unit cells where K^+ ion can enter, and the number of K^+ ions vacant lattice points increase as the composition x becomes smaller than 2.0. Figure 8 is a model (sample) of K^+ ion distribution. The ion is not arranged systematically. Like Byström and his colleagues [4], who hypothesized the position of barium in hollandite, we should envision it as being distributed from a statistical viewpoint. Migration of K^+ ion in the direction of the a axis is virtually ruled out, for it mainly moves in the direction of the c axis through vacant lattice points. Hence, the smaller the composition x , the greater the K^+ ion conductivity.

The conductivity reflected in Figure 6 is in accord with these findings relative to the tunnel structure: the smaller the composition x , the greater the conductivity. In the case of $K_{1.6}Mg_{0.8}Ti_{7.2}O_{16}$, having a tetragonal single phase boundary, $10^{-4} \text{ mho} \cdot \text{cm}^{-1}$ at 300°C , a very large value in terms of K^+ ion conductivity was obtained.

A comparison of conductivity of three types of crystals containing potassium — KCl , $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ and $KAl_{11}O_{17}$ (potassium- β alumina) — showed, at 300°C , 10^{-7} [6], 10^{-4} and $10^{-3} \text{ mho} \cdot \text{cm}^{-1}$ [10] respectively. In the former, K^+ ion conductivity was through the Schottky type K^+ ion vacant lattice points; in the center, through the vacant lattice points in the one-dimensional tunnel structure as previously explained; and in the latter, through vacant lattice points in the two-dimensional

layer structure.[11] From these comparisons, it is clear that the contribution of the hollandite type tunnel structure to K⁺ion conductivity is small compared to that of the β -alumina type layer structure. However, in contrast to the requirement of higher temperature than 1700°C and the process to prevent the evaporation of potassium in order to obtain good sinters from $KAl_{11}O_{17}$, the outstanding characteristic of $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ is that it provides good sinters from $KAl_{11}O_{17}$ at several hundred degrees lower temperature minus the problem of potassium evaporation. Further, the contribution of the hollandite type tunnel structure to K⁺ion conductivity is much larger than that of the Schottky type, defective point structure. Plans are currently being formulated for a further study as a detailed qualitative discussion concerning multi-crystalline sinters would require research into the crystalline structure and energy relative to ion migration.

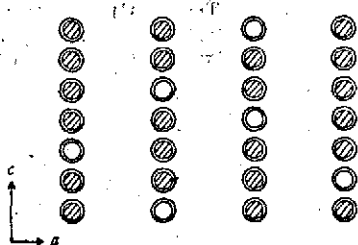


Fig. 8 Model to potassium ion distribution in hollandite type compound $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ projected on (100)
Open circles denote potassium ion vacancy and closed circles potassium ion.

4. Summary

The following observations were made as a result of this research into the formation of sintered oxides of the hollandite type structure $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ and their ionic conductivity.

(1) Good sinters are obtainable by firing K_2CO_3 , MgO and TiO_2 for five hours at 1200°C after prefiring for 10 hours at 950°C.

(2) The range of tetragonal single phase is $1.6 \leq x \leq 2.0$.

(3) Conductivity of single phase sinter is 10^{-5} – 10^{-4} mho·cm⁻¹ at 200–400°C.

(4) Conduction seed is K⁺ion.

(5) A study of K⁺ion conductivity and hollandite structure led us to presume that the tunnel plays a major role in K⁺ion conductivity.

REFERENCES

1. Takahashi, T. J. Appl. Electrochem., 3, 1973, p. 79.
2. Kiriyama, R., H. Kiriyama. Structural Inorganic Chemistry, Kyoritsu Publications, 1964, p. 246.
3. Bayer, G., W. Hoffman. Amer. Mineral, 51, 1966, p. 511.
4. Bystrom, A., A.M. Bystrom, Acta Cryst., 3, 1950, p. 146.
5. Dryden, J.S., A.D. Wadsley. Trans. Faraday Soc., 54, 1958, p. 1574.
6. Kelkhoff, F. Z. Phys., 130, 1951, p. 449.
7. Tubandt, C. Handbook of Experimental Physics, 12, 1932, p. 383.
8. Mizuta, S., H. Yanagida, Denikagaka, 40, 1972, p. 787.
9. Singer, J, H.E. Kautz, W.L. Fielder, J.S. Fordyce, NASA Tech. Note D-7157, 1973.
10. Yao, Y.F., J.T. Kummer. J. Inorg. Nucl. Chem., 29, 1967, p. 2453.
11. van Gool, W. "Fast Ion Transport in Solids", North-Holland Pub. Inc., Amsterdam, 1973, p. 557.

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